



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07C 17/278, 17/275, 19/16, 41/30, 43/12, C07B 37/02	A1	(11) International Publication Number: WO 97/44300 (43) International Publication Date: 27 November 1997 (27.11.97)
(21) International Application Number: PCT/US97/08166 (22) International Filing Date: 14 May 1997 (14.05.97) (30) Priority Data: 60/018,087 22 May 1996 (22.05.96) US (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): YANG, Zhen-Yu [CN/US]; 2609 Marhill Drive, Wilmington, DE 19810 (US). (74) Agent: HEISER, David, E.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: CN, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>

(54) Title: PROCESS USING CF_2I_2 AND OLEFINS FOR PRODUCING DIIDO FLUOROCOMPOUNDS, AND PRODUCTS THEREOF

(57) Abstract

A process is disclosed for making diiodofluorinated compounds of the formula $\text{ICF}_2(\text{A})_n\text{I}$ wherein n is an integer of at least 1 and each A is $\text{CX}_1\text{Y}\text{CQZ}$ wherein each X , Y , Q and Z are each independently selected from the group consisting of H , F , Cl , R_F and OR_F , and R_F is a perfluoroalkyl group or perfluorinated polyether group wherein one or more of the fluorines is optionally replaced by a substituent selected from the group consisting of chlorine, bromine, iodine, hydrogen, sulfonyl fluoride, nitrile, ester, acyl chloride and acyl fluoride. The process involves reacting an olefin of the formula $\text{CX}_1\text{Y} = \text{CQZ}$ with CF_2I_2 at a temperature in the range of from about 120°C to 240°C . Diiodofluorinated compounds of the formula $\text{ICF}_2\text{CH}_2\text{CHR}_\text{F}\text{I}$ are also disclosed.

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

TITLEPROCESS USING CF_2I_2 AND OLEFINS FOR PRODUCING DIIDO
FLUOROCOMPOUNDS, AND PRODUCTS THEREOFFIELD OF THE INVENTION

5 This invention relates to diiodofluorinated compounds and their production, and more particularly to using CF_2I_2 and olefinic compounds as reactants for producing diiodofluorinated compounds.

BACKGROUND

10 Diiodoperfluoroalkanes are useful as chain transfer reagents for fluoroelastomers and in the free radical polymerization of fluorinated vinyl monomers. See U.S. Patent Nos. 4,243,770 and 4,361,678. The reaction of CF_2I_2 with olefins allows the stepwise addition to the chain, thereby providing controlled chain growth. The production of these diiodoperfluoroalkanes at relatively high yields has been hampered in the past by the lack of a method by
15 which to produce relatively high yield and purity CF_2I_2 . However, as described in commonly held U.S. Patent Application No. 60/012,160, filed February 23, 1996, CF_2I_2 can be produced in sufficiently high yields to facilitate the reactions described below.

Commonly held U.S. Patent No. 5,504,248 describes the production of
20 diiodofluoroalkanes by reacting I_2 with hexafluorocyclopropane. This process involves a relatively complex ring-opening reaction, and uses relatively expensive starting materials.

Elsheimer, et al., J. Org. Chem. 1984, 49, pp. 205-207, discloses reactions of CF_2I_2 with hydrocarbon olefins to produce iododifluoroalkenes via photolysis,
25 or diiododifluoroalkanes via reactions catalyzed by peroxide at temperatures less than 100°C . The use of peroxides to form the diiododifluoroalkanes could result in the production of other reaction products, which would have to be separated from the desired products, thus adding an additional step, as well as the associated costs involved with such purification.

30 Many citations are found throughout the literature describing diiodofluorinated compounds, but interest continues in developing new, efficient processes for producing selected diiodofluorinated compounds.

SUMMARY OF THE INVENTION

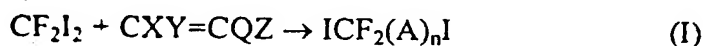
A process is provided for making diiodofluorinated compounds of the
35 formula $\text{ICF}_2(\text{A})_n\text{I}$ wherein n is an integer of at least 1 and each A is $\text{CX}_1\text{Y}_1\text{CQ}_1\text{Z}_1$ wherein each X, Y, Q, and Z are each independently selected from the group consisting of H, F, Cl, R_F and OR_F , and R_F is a perfluoroalkyl group containing 1 to 20 carbon atoms or a perfluorinated polyether group containing from 2 to

20 carbon atoms wherein one or more of the fluorines of said perfluoroalkyl or perfluorinated polyether group is optionally replaced by a substituent selected from the group consisting of chlorine, bromine, iodine, hydrogen, sulfonyl fluoride, nitrile, ester, acyl chloride and acyl fluoride. The process comprises
5 reacting an olefin of the formula $CXY=CQZ$ with CF_2I_2 at a temperature in the range of from about 120°C to 240°C.

Diiodofluorinated compounds of the formula $ICF_2CH_2CHR_FI$, where R_F is as indicated above, are also provided in accordance with this invention.

DETAILED DESCRIPTION

10 This invention provides a process by which CF_2I_2 is reacted with olefins to produce diiodofluorinated compounds, generally described in Equation (I) below:



15 In Equation (I), A represents $(CXYCQZ)$, and X, Y, Q and Z are each independently H, F, Cl, R_F or OR_F , and preferably at least one of X, Y, Q and Z is F. The number of repeat units of A, as represented by n in Equation (I) is 1 or greater and is preferably from 1 to about 5, more preferably from 1 to 3. Of note
20 are embodiments where n is 1; embodiments where n is 2; and embodiments where n is 3.

The process represented by Equation (I) takes place at an elevated temperature. It has been found in accordance with this invention that when conducted at temperatures of about 120°C or above, the reaction needs no
25 chemical catalyst or initiator to proceed. Indeed, the process of this invention is typically conducted in the substantial absence of a catalyst or initiator. By "substantial absence of catalyst or initiator" is meant that the reaction would effectively proceed even in the absence of any catalyst or initiator which might be added. By "catalyst or initiator" is meant materials or chemicals such as, for
30 example, peroxides or azo compounds, which have been previously required to produce diiodofluorinated compounds at lower temperatures.

The temperature range is generally between about 120°C and about 240°C, and is preferably between about 170°C and about 190°C. The process can take place in the liquid or gas phase. Liquid phase reactions may be conducted in
35 solution in inert solvents such as, for example, fluorocarbons, fluorochlorocarbons and hydrofluorocarbons, or (preferably) may be conducted neat. Although not necessary, if the reaction is carried out in the liquid state, moderate agitation is preferred. It is also preferred that oxygen and water are excluded from the

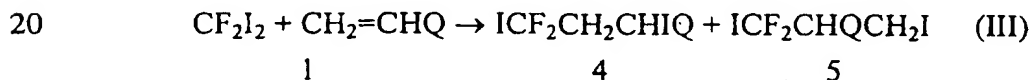
reaction, and it may be convenient to carry out the reaction under an inert gas blanket, such as nitrogen.

Pressure is not critical, autogenous pressure (of all the ingredients) being generally the convenient operation pressure. Typically, the reaction is conducted at pressure within the range of from about 20 psi (about 138 Pa) to about 1000 psi (about 6900 Pa). Non-limiting examples of reaction vessels include shaker tubes, tanks, autoclaves and reactors.

It is noted that for each addition of olefinic starting material, the unit A can have either of two orientations, with either carbon involved with the olefinic bond, attaching to the end carbon of the iodo reactant. Accordingly, where the carbons involved with the olefinic bond are differently substituted, the addition of each A group can result in either of two products. Thus for example, when n is 1, the reaction can be represented as:

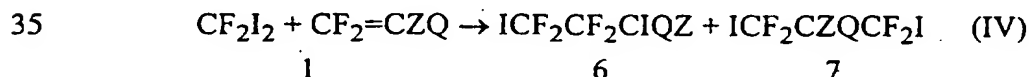


When X, Y and Z are each H in Equation (II), the reaction may be represented by Equation (III) below:



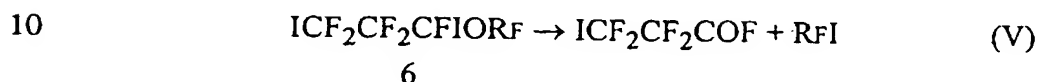
Both fluorinated or non-fluorinated olefins, as determined by the composition of Q, give relatively good yields of adducts. When reacted with ethylene, a relatively higher yield of adduct 4 is obtained, as described in Example 1 below. A mixture of regioisomers 4 and 5 is, however, formed with propylene and vinyl fluoride (Examples 2 and 8, respectively). Fluoroalkyl substituted olefins or fluorinated polyether substituted olefin such as $\text{CH}_2=\text{CHR}_\text{F}$ where R_F is highly fluorinated (Examples 3 and 4) also undergo an addition reaction with CF_2I_2 to give 4 exclusively. Examples of highly fluorinated R_F groups include $\text{CF}_2\text{CF}_2\text{Br}$, $\text{CF}_2\text{CF}_2\text{I}$, and perfluoroalkyl groups (e.g., C_4F_9 , C_6F_{13} and C_8F_{17} groups).

Preferably at least one of X, Y, Z and Q is F. When X and Y are each F in Equation (I), the reaction may be represented by Equation (IV) below:

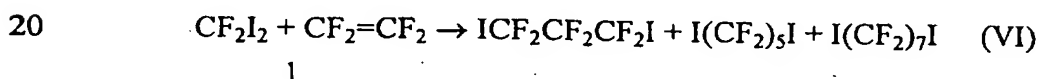


Of note are embodiments of Equation (IV) where Q is F, H, R_F or OR_F and
embodiments where Z is F. Fluorinated olefins such as CF₂=CFH, CF₂=CFCF₃
40 and CF₂=CH₂ give mixtures of regioisomers 6 and 7. Unlike other perfluoroalkyl
iodides, CF₂I₂ cleanly adds to perfluorovinyl ethers of the formula CF₂=CFOR_F

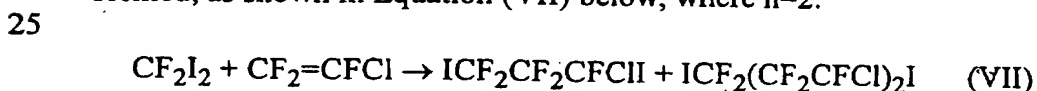
to give compound 6 ($Q = OR_F$), along with small amounts of compound 7 ($Q = OR_F$). The functional groups such as ester, sulfonyl fluoride and nitrile in the vinyl ethers do not interfere with the addition reaction, so that various functional diiodocompounds may be prepared, as found in Examples 12-15. When the reaction mixture of fluorovinyl ethers and CF_2I_2 is subjected to prolonged heating, as in Examples 12 and 15, the initially formed compound 6, in Equation (V) below, where $Q = OR_F$, decomposes to ICF_2CF_2COF and R_FI (see also U.S. Patent No. 5,504,248).



The addition of R_FI to tetrafluoroethylene (TFE), as shown in Example 5, gives a broad distribution of telomers. See also Chemistry of Organic Fluorine Compounds, 2nd Ed. M. Hudlicky, 1992, p. 420-427). While CF_2I_2 reacts with TFE, the main product is a 1:1 adduct ($ICF_2CF_2CF_2I$) with only small amounts of 1:2 adduct ($I(CF_2)_5I$) and trace of 1:3 adduct ($I(CF_2)_7I$), as shown in Equation (VI) below:



When $CF_2=CFCl$ is reacted with CF_2I_2 , a mixture of 1:1 and 1:2 adducts is formed, as shown in Equation (VII) below, where $n=2$.



Other higher homologs are also formed (e.g., n is 3, 4, etc.). In general, higher ratios of olefinic starting materials to CF_2I_2 yield higher telomers (i.e., n is higher). The degree of telomerization is limited by product solidification. Preferably, the ratio of olefinic starting material to CF_2I_2 is from about 1:1 to 5:1.

The diiodocompounds formed by the instant process, when one of X, Y, Z or Q is a functional group as represented by R_F or OR_F , may be used to chain extend or graft the resulting polymer onto another polymer, or to react to form a specific chain end which may act to change the polymer's surface properties. One example of this would be the production of a potential surfactant material when R_F is a fluorinated ester or fluorinated sulfonyl group.

Compounds provided by this invention include compounds where each A is (CH_2CHR_F) . Of note are compounds of this type having the formula

$$40 \quad ICF_2CH_2CHR_FI.$$

In the Examples below, unless otherwise specified, all reagents were used as received from Aldrich Chemical Co., Milwaukee, WI. CF_2I_2 was made according to the procedure as described in co-pending U.S. Patent Application No. 60/012,160.

5 Gas chromatography (GC) was performed on an HP 5890 II Plus gas chromatograph (Hewlett Packard, Wilmington, DE), using a 20% OV-210 column (Supelco, Bellefonte, PA), with an initial temperature of 50°C , a final temperature of 250°C , and a rate of $15^\circ\text{C}/\text{min}$. The ^1H and ^{19}F nuclear magnetic resonance (NMR) data were obtained using a GE Plus NMR spectrometer (General Electric, 10 Schenectady, NY). All measurements are relative to deuterated chloroform (CDCl_3). Ratios given are those for peak areas by GC or molar ratios based on NMR data as designated in the specific examples. High resolution mass spectrometry (HRMS) was done using a Micromass-7070H (VG Analytical, Manchester, UK).

15 The reaction products were obtained by distillation, and their boiling points (bp, $^\circ\text{C}$) were obtained. Elemental analyses were obtained by routine methods.

The following abbreviations are used in the Examples below:

s = singlet NMR peak
20 d = doublet NMR peak
t = triplet NMR peak
m = multiplet NMR peak

EXAMPLE 1

Reaction of CF_2I_2 with ethylene

25 A 75 mL of shaker tube was charged with 30.5 g of CF_2I_2 and cooled to -78°C . The tube was evacuated and then 4.0 g of ethylene was added. After the tube was heated at 185°C for 5 hour, 30.3 g of crude product was obtained which was distilled to give 27.3 g of adduct with 100% GC purity, bp $94-95^\circ\text{C}/50$ mmHg. ^{19}F NMR: -39.1 (t, $J = 14.3$ Hz); ^1H NMR: 3.21 (t, $J = 7.3$ Hz, 2H), 30 2.95 (m, 2H). HRMS: calcd for $\text{C}_3\text{H}_4\text{F}_2\text{I}_2$: 331.8371. Found: 331.8336. Anal: calcd for $\text{C}_3\text{H}_4\text{F}_2\text{I}_2$: C, 10.86; H, 1.21; F, 11.45; I, 76, 48. Found: C, 10.84; H, 1.25; F, 11.59; I, 75.96.

EXAMPLE 2

Reaction of CF_2I_2 with propylene

35 A 75 mL of shaker tube was charged with 30.5 g of CF_2I_2 and cooled to -78°C . The tube was evacuated and then 5.0 g of propylene was added. After the tube was heated at 185°C for 5 hour, 31.6 g of crude product was obtained which was distilled to give 28.7 g of product, bp $106-107^\circ\text{C}/4.8$ mmHg. GC and NMR

indicated a mixture of $\text{ICF}_2\text{CH}_2\text{CHICH}_3$ and $\text{ICH}_2\text{CH}(\text{CF}_2\text{I})\text{CF}_3$ in a ratio of 13 to 1. ^{19}F NMR: for major product: -35.4 (ddd, $J = 173 \text{ Hz}$, $J = 18.4 \text{ Hz}$, $J = 8.7 \text{ Hz}$, 1F), -38.3 (dt, $J = 173 \text{ Hz}$, $J = 16.4 \text{ Hz}$, 1F). ^1H NMR: 4.35 (m, 1H), 3.28 (m, 1H), 2.90 (m, 1H), 2.00 (d, $J = 7.0 \text{ Hz}$, 3H). HRMS: calcd for $\text{C}_4\text{H}_7\text{F}_2\text{I}_2$:

- 5 345.8527. Found: 345.8565 for $\text{ICF}_2\text{CH}_2\text{CHICH}_3$ and 345.8510 for $\text{ICH}_2\text{CH}(\text{CF}_2\text{I})\text{CH}_3$. Anal: calcd for $\text{C}_4\text{H}_7\text{F}_2\text{I}_2$: C, 13.89; H, 1.75; F, 10.98; I, 73.38. Found: C, 13.99; H, 1.98; F, 10.80; I, 73.34.

EXAMPLE 3

Reaction of CF_2I_2 with 4-bromo-3,3,4,4-tetrafluorobutene-1

- 10 A 75 mL of shaker tube was charged with 30.5 g of CF_2I_2 and 21.0 g of $\text{BrCF}_2\text{CF}_2\text{CH}=\text{CH}_2$ and cooled to -78°C . The tube was evacuated and then heated at 180°C for 2.5 hour. 31.6 g of crude product was obtained which was washed with aqueous Na_2SO_3 solution and distilled to give 28.7 g of $\text{ICF}_2\text{CH}_2\text{CHICF}_2\text{CF}_2\text{Br}$, bp $53^\circ\text{C}/19 \text{ mmHg}$. ^{19}F NMR: -36.7 (ddd, $J = 176.1$
- 15 Hz, $J = 16.2 \text{ Hz}$, $J = 7.1 \text{ Hz}$, 1F), -39.7 (dt, $J = 176 \text{ Hz}$, $J = 15.8 \text{ Hz}$, 1F), -59.9 (dd, $J = 178.6 \text{ Hz}$, $J = 7.6 \text{ Hz}$, 1F), -61.0 (dd, $J = 178.6 \text{ Hz}$, $J = 5.6 \text{ Hz}$, 1F), -94.6 (dt, $J = 260.6 \text{ Hz}$, $J = 7.2 \text{ Hz}$, 1F), -109.8 (ddd, $J = 261.0 \text{ Hz}$, $J = 18 \text{ Hz}$, $J = 7.4 \text{ Hz}$, 1F).

EXAMPLE 4

Reaction of CF_2I_2 with 4-iodo-3,3,4,4-tetrafluorobutene-1

- 20 A 75 mL of shaker tube was charged with 42.3 g of 1:1 mixture of CF_2I_2 and $\text{ICF}_2\text{CF}_2\text{CH}=\text{CH}_2$ and cooled to -78°C . The tube was evacuated and then heated at 180°C for 2.5 hour. 36 g of crude product was obtained, which was washed with aqueous Na_2SO_3 solution and distilled to give 23.5 g of $\text{ICF}_2\text{CH}_2\text{CHICF}_2\text{CF}_2\text{I}$, bp $118-120^\circ\text{C}/10 \text{ mmHg}$. ^{19}F NMR: -36.7 (ddd, $J =$
- 25 175.5 Hz, $J = 16.0 \text{ Hz}$, $J = 7.7 \text{ Hz}$, 1F), -39.6 (dt, $J = 175.5 \text{ Hz}$, $J = 16.0 \text{ Hz}$, 1F), -54.8 (ddt, $J = 202.2 \text{ Hz}$, $J = 7.3 \text{ Hz}$, $J = 2.3 \text{ Hz}$, 1F), -56.0 (dd, $J = 203.0 \text{ Hz}$, $J = 7.0 \text{ Hz}$, 1F), -88.3 (dt, $J = 261.0 \text{ Hz}$, $J = 7.0 \text{ Hz}$, 1F), -106.2 (ddd, $J = 261.0 \text{ Hz}$, $J = 19 \text{ Hz}$, $J = 8.4 \text{ Hz}$, 1F).

EXAMPLE 5

Reaction of CF_2I_2 with tetrafluoroethylene

- 30 A 400 mL of shaker tube was charged with 152 g of CF_2I_2 and cooled to -78°C . After the tube was evacuated and then heated to 185°C , 20 g of TFE was added and the tube kept at 185°C for 2 hours. Additional 20 g of TFE was added and the tube was kept for 2 hours. Finally, 10 g of TFE was added and the tube
- 35 kept for 6 hours. 192.3 g of crude products were obtained and GC indicated that a mixture of 82% $\text{I}(\text{CF}_2)_3\text{I}$ and 7% $\text{I}(\text{CF}_2)_5\text{I}$. Distillation gave 169.6 g of $\text{I}(\text{CF}_2)_3\text{I}$ with 2.5% of $\text{I}(\text{CF}_2)_5\text{I}$, bp $76-80^\circ\text{C}/150 \text{ mmHg}$, and 13.1 g of high boiling residue containing 20% $\text{I}(\text{CF}_2)_3\text{I}$, 70% $\text{I}(\text{CF}_2)_5\text{I}$ and 5% $\text{I}(\text{CF}_2)_7\text{I}$. ^{19}F NMR for $\text{I}(\text{CF}_2)_3\text{I}$:

-58.2 (t, $J = 4.7$ Hz, 4F), -105.2 (t, $J = 4.7$ Hz, 2F); for $\text{I}(\text{CF}_2)_5\text{I}$: -59.4 (t, $J = 4.6$ Hz, 4F), -113.6 (s, 4F), -120.6 (m, 2F).

EXAMPLE 6

Reaction of CF_2I_2 with trifluoroethylene

- 5 A 75 mL of shaker tube was charged with 30.5 g of CF_2I_2 and cooled to -78°C . The tube was evacuated and then 16.0 g of trifluoroethylene was added. After the tube was heated at 185°C for 10 hour, GC indicated 70% of conversion and 26.3 g of crude product was obtained which was washed with aqueous Na_2SO_3 solution and distilled to give 1.5 g of 55% pure of adduct, 2.5 g of 84%
 10 pure adduct and 12.8 g of pure product bp $83^\circ\text{C}/80$ mmHg. ^{19}F NMR and GC indicated a mixture $\text{ICF}_2\text{CHFCF}_2\text{I}$ and $\text{ICF}_2\text{CF}_2\text{CHF}$ in a ratio of 1.5 to 1. ^{19}F NMR: $\text{ICF}_2\text{CHFCF}_2\text{I}$: -52.6 (dm, $J = 207.8$ Hz, 2F), -54.8 (dm, $J = 207.8$ Hz, 2F), -176.2 (m, 1F); $\text{ICF}_2\text{CF}_2\text{CHF}$: -57.9 (dm, $J = 207.8$ Hz, 1F), -59.8 (dt, $J = 207.8$ Hz, $J = 6.5$ Hz, 1F), -101.0 (ddt, $J = 273.1$ Hz, $J = 32.3$ Hz, $J = 6.3$ Hz, 1F),
 15 -116.3 (dm, $J = 273.1$ Hz, 1F), -165.7 (m, 1F). HRMS: calcd. for $\text{C}_3\text{HF}_5\text{I}_2$: 385.8088. Found: 385.8023. Anal: calcd for $\text{C}_3\text{HF}_5\text{I}_2$: C, 9.34; H, 0.26; F, 24.62; I, 65.78. Found: C, 9.25; H, 0.27; F, 24.39; I, 65, 81.

EXAMPLE 7

Reaction of CF_2I_2 with vinylidene fluoride

- 20 A 75 mL of shaker tube was charged with 30.5 g of CF_2I_2 and cooled to -78°C . The tube was evacuated and then 10.0 g of $\text{CF}_2=\text{CH}_2$ was added. After the tube was heated at 185°C for 8 hour, GC indicated 10% CF_2I_2 and 79.5% of adduct (area ratio). 35.1 g of crude products were obtained which was distilled to give 4.1 g of 50% pure of adduct and 26.4 g of pure adduct, bp
 25 $80\text{--}81^\circ\text{C}/60$ mmHg. ^{19}F NMR and GC indicated a mixture $\text{ICF}_2\text{CH}_2\text{CCF}_2\text{I}$ and $\text{ICF}_2\text{CF}_2\text{CH}_2\text{I}$ in a ratio of 27.6 to 1. ^{19}F NMR: $\text{ICF}_2\text{CH}_2\text{CF}_2\text{I}$: -39.6 (m); $\text{ICF}_2\text{CF}_2\text{CH}_2\text{I}$: -59.6 (t, $J = 4$ Hz, 2F), -101.5 (t, $J = 16.4$ Hz, 2F). HRMS: Calcd for $\text{C}_3\text{H}_2\text{F}_4\text{I}_2$: 367.8182. Found: 367.8168 for $\text{ICF}_2\text{CH}_2\text{CF}_2\text{I}$; 367.8150 for $\text{ICF}_2\text{CF}_2\text{CH}_2\text{I}$. Anal: calcd for $\text{C}_3\text{H}_2\text{F}_4\text{I}_2$: C, 9.80; H, 0.55; I, 69.00. Found: C,
 30 9.76; H, 0.62; I, 68.48.

EXAMPLE 8

Reaction of CF_2I_2 with vinyl fluoride

- A 75 mL of shaker tube was charged with 30.5 g of CF_2I_2 and cooled to -78°C . The tube was evacuated and then 6.0 g of vinyl fluoride was added. After
 35 the tube was heated at 185°C for 5 hour, GC indicated 90% of conversion and 27.8 g of crude product was obtained which was distilled to give 4.9 g of 55% pure of adduct and 17.1 g of pure product, bp $87\text{--}89^\circ\text{C}/50$ mmHg. ^{19}F NMR and GC indicated a mixture $\text{ICF}_2\text{CH}_2\text{CCFH}$ and $\text{ICF}_2\text{CFHCH}_2\text{I}$ in a ratio of 8.6 to 1.

^{19}F NMR: $\text{ICF}_2\text{CH}_2\text{CHFI}$: -37.6 (dm, $J = 178.5$ Hz, 1F), -40.33 (dm, $J = 178.5$ Hz, 1F), -144.7 (m, 1F); $\text{ICF}_2\text{CFHCH}_2\text{I}$: -51.8 (ddd, $J = 195.5$ Hz, $J = 21.0$ Hz, $J = 7.4$ Hz, 1F), -56.3 (ddd, $J = 196$ Hz, $J = 21.7$ Hz, $J = 7.3$ Hz, 1F), -176.8 (m, 1F).
 HRMS: calcd for $\text{C}_3\text{H}_3\text{F}_3\text{I}_2$: 349.8280. Found: 349.8391 for $\text{ICF}_2\text{CH}_2\text{CFHI}$;
 5 349.8307 for $\text{ICF}_2\text{CFHCH}_2\text{I}$. Anal: calcd for $\text{C}_3\text{H}_3\text{F}_3\text{I}_2$: C, 10.30; H, 0.86.
 Found: C, 10.26; H, 1.00.

EXAMPLE 9

Reaction of CF_2I_2 with hexafluoropropylene

A 75 mL of shaker tube was charged with 45.6 g of CF_2I_2 and cooled to
 10 -78°C. The tube was evacuated and then 24.0 g of hexafluoropropylene was
 added. After the tube was heated at 185°C for 12 hour, GC indicated 55% of
 conversion and 40.1 g of crude were washed with aqueous Na_2SO_3 solution and
 then distilled to give 6.2 g of 82% pure of CF_2I_2 , 2.7 g of a mixture of 60% of
 CF_2I_2 and 28% of $\text{ICF}_2\text{CF}_2\text{CFICF}_3$, bp 40-63°C/95 mmHg, 3.0 g of a mixture of
 15 23% of CF_2I_2 and 62% of $\text{ICF}_2\text{CF}_2\text{CFICF}_3$, bp 64-71°C/95 mmHg and 10.6 g of
 93% pure $\text{ICF}_2\text{CF}_2\text{CFICF}_3$, bp 74-76°C/95 mmHg. HRMS: calcd for $\text{C}_4\text{F}_8\text{I}_2$:
 453.7962. Found: 453.7915 for $\text{ICF}_2\text{CF}_2\text{CFICF}_3$; 3452.7967 for $(\text{ICF}_2)_2\text{CFCF}_3$.

EXAMPLE 10

Reaction of CF_2I_2 with perfluoromethyl vinyl ether

A 75 mL of shaker tube was charged with 30.5 g of CF_2I_2 and cooled to
 20 -78°C. The tube was evacuated and then 22.0 g of perfluoromethyl vinyl ether
 was added. After the tube was heated at 185°C for 3.5 hour, GC indicated 76% of
 conversion and 37.2 g of crude products were distilled to give 13.8 g of 47.6% of
 CF_2I_2 and 46.7% of adduct, bp 50-79°C/100 mmHg and 18.4 g of 99% pure
 25 adduct, bp 87-89°C/50 mmHg. ^{19}F NMR and GC indicated a mixture
 $\text{ICF}_2\text{CF}_2\text{CFIOCF}_3$ and $(\text{ICF}_2)_2\text{CFOCF}_3$ in a ratio of 12 to 1. ^{19}F NMR for
 $\text{ICF}_2\text{CF}_2\text{CFIOCF}_3$: -55.0 (dm, $J = 204.1$ Hz, 1F), -55.3 (d, $J = 11.3$ Hz, 3F),
 -58.4 (ddm, $J = 205$ Hz, $J = 26.4$ Hz, 1F), -68.0 (m, 1F), -102.6 (dt, $J = 276.2$ Hz, J
 = 7.7 Hz, 1F), -104.2 (dt, $J = 276.4$ Hz, $J = 7.2$ Hz, 1F); for $(\text{ICF}_2)_2\text{OCF}_3$: -51.7
 30 (m, 3F), -53.9 (m, 4F), -124.2 (m, 1F); HRMS: calcd for $\text{C}_4\text{F}_8\text{I}_2\text{O}$: 469.7911.
 Found: 469.7930 for $\text{ICF}_2\text{CF}_2\text{CFIOCF}_3$; 469.7967 for $(\text{ICF}_2)_2\text{CFOCF}_3$.

EXAMPLE 11

Reaction of CF_2I_2 with perfluoropropyl vinyl ether

A 75 mL of shaker tube was charged with 30.5 g of CF_2I_2 and cooled to
 35 -78°C. The tube was evacuated and then 60.0 g of perfluoropropyl vinyl ether
 was added. After the tube was heated at 185°C for 3.5 hour, 78.5 g of crude
 products were distilled to give 29.0 g of perfluoropropyl vinyl ether; 6.2 g of 72%
 pure of adduct, bp 30-80°C/40 mmHg; 27.6 g of pure adduct, bp

83-84°C/40 mmHg; and 4.4 g of 68% pure adduct, bp 85°C/40 mmHg to 74°C/15 mmHg. Yield 79%. ^{19}F NMR and GC indicated a mixture $\text{ICF}_2\text{CF}_2\text{CFIOCF}_2\text{CF}_2\text{CF}_3$ and $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}_2\text{CF}_3$ in a ratio of 85.4 to 13.6. ^{19}F NMR for $\text{ICF}_2\text{CF}_2\text{CFIOCF}_2\text{CF}_2\text{CF}_3$: -55.3 (d, $J = 204.6$ Hz, 1F), -58.8 (ddd, $J = 204.6$ Hz, $J = 27$ Hz, $J = 6.3$ Hz, 1F), -68.7 (m, 1F), -81.3 to -81.9 (m, 4F), -90.7 (d, $J = 147.6$ Hz, 1F), -102.4 (dt, $J = 276.7$ Hz, $J = 8$ Hz, 1F), -104.4 (dt, $J = 276.6$ Hz, $J = 7.5$ Hz, 1F), -130.4 (s, 2F). $(\text{ICF}_2)_2\text{OCF}_2\text{CF}_2\text{CF}_3$: -53.8 (m, 4F), -79.4 (m, 2F), -81.3 (M, 3F), -122.3 (m, 1F), -129.3 (M, 2F). HRMS: calcd for $\text{C}_6\text{F}_{12}\text{I}_2\text{O}$: 569.7847. Found: 442.8824 for $\text{ICF}_2\text{CF}_2\text{CFIOCF}_2\text{CF}_2\text{CF}_3$ -I; 569.7796 for $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}_2\text{CF}_3$. Anal: calcd for $\text{C}_6\text{F}_{12}\text{I}_2\text{O}$: C, 12.65; I, 44.55. Found: C, 12.72; I, 44.23.

EXAMPLE 12

Reaction of CF_2I_2 with $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$

A 240 mL of shaker tube was charged with 30.5 g of CF_2I_2 and 60.0 g of $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$ and cooled to -78°C. After being evacuated at -78°C, the tube was heated at 185°C for 3.5 hour. 82.2 g of a mixture of 5% of $\text{ICF}_2\text{CF}_2\text{COF}$, 4% of CF_2I_2 , 31% of $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$, 9% $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$ and 51% adduct were obtained (GC area). Distillation gave 12.3 g of mainly $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$, bp 40-88°C/60 mmHg, 8.6 g of material containing 45% $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$ and 55% of $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$, bp 82°C/50 mmHg to 102°C/4 mmHg, and 45.9 g of adduct, bp 103-110°C/3 mmHg. The adduct was a mixture of $\text{ICF}_2\text{CF}_2\text{CFIOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$ and $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$.

EXAMPLE 13

Reaction of CF_2I_2 with $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$

A 240 mL of shaker tube was charged with 30.5 g of CF_2I_2 and 45.0 g of $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$ and cooled to -78°C. After being evacuated at -78°C, the tube was heated at 185°C for 4 hour. 67.8 g of crude products were obtained. Distillation gave 15 g of mainly $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$, bp 85-100°C, 37.6 g of adduct, bp 115-116°C/30 mmHg. The adduct was a mixture of $\text{ICF}_2\text{CF}_2\text{CFIOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$ and $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$ in a ratio of 5.7 to 1. ^{19}F NMR for $\text{ICF}_2\text{CF}_2\text{CFIOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$: -55.5 (d, $J = 205.2$ Hz, 1F), -58.9 (ddd, $J = 205.5$ Hz, $J = 27.3$ Hz, $J = 6.0$ Hz, 1F), -69.4 (m, 1F), -79.1 to -80.4 (m, 4F), -84.1 to -85.2 (m, 2F), -90.0 (dm, $J = 152.5$ Hz, 1F), -102.0 (dm, $J = 277.7$ Hz, 1F), -104.5 (dm, $J = 277.7$ Hz, 1F), -108.6 (m, 2F), -145.1 (t, $J = 21.2$ Hz, 0.5F),

-145.6 (t, J = 21.3, Hz, 0.5F); for $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$: -53.1 (m, 2F), -54.5 (m, 2F), -78.2 (m, 2F), -80.1 (m, 3F), -84.1 (m, 2F), -108.4 (m, 2F), -121.2 (m, 1F), -144.6 (m, 1F). HRMS: Calcd for $\text{C}_9\text{F}_{15}\text{I}_2\text{NO}_2$ -I, 565.8734. Found: 565.8716 (M^+ -I). Anal: calcd for $\text{C}_9\text{F}_{15}\text{I}_2\text{NO}_2$: C, 15.60; N, 2.02; I, 36.63. Found: C, 16.26; N, 2.02; I, 35.74.

EXAMPLE 14

Reaction of CF_2I_2 with $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$

A 240 mL of shaker tube was charged with 30.5 g of CF_2I_2 and 50.0 g of $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ and cooled to -78°C . After being evacuated at -78°C , the tube was heated at 185°C for 4 hour. 71.3 g of crude products were obtained. Distillation gave 10.3 g of CF_2I_2 , 42 g of adduct, 95-97°C/5.4 mmHg. The adduct was a mixture of $\text{ICF}_2\text{CF}_2\text{CFIOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ and $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ in a ratio of 5.2 to 1. ^{19}F NMR for $\text{ICF}_2\text{CF}_2\text{CFIOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$: +45.3 (m, 1F), -55.6 (d, J = 204.7 Hz, 1F), -58.9 (ddd, J = 204.7 Hz, J = 27.2 Hz, J = 6.3 Hz, 1F), -69.3 (m, 1F), -79.3 to -80.2 (m, 4F), -89.8 (dm, J = 144.3 Hz, 1F), -101.9 (dm, J = 277.9 Hz, 1F), -104.6 (dt, J = 277.8 Hz, J = 7.7 Hz, 1F), -112.2 (m, 2F), -145.4 (m, 1F); for $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$: -53.2 (m, 2F), -54.5 (m, 2F), -78.2 (m, 2F), -80.1 (m, 5F), -112.4 (m, 2F), -121.2 (m, 1F), -144.6 (m, 1F).

EXAMPLE 15

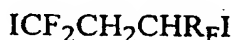
Reaction of CF_2I_2 with

$\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ at high temperature

A 240 mL of shaker tube was charged with 30.6 g of CF_2I_2 and 50.0 g of $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ and cooled to -78°C . After being evacuated at -78°C , the tube was heated at 185°C for 4 hour and 240°C for 8 hours. 71.5 g of crude products were obtained. GC indicated a mixture of $\text{ICF}_2\text{CF}_2\text{COF}$, $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$, and $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ in a ratio of 4.1:6.6:1 (area ratio). Distillation gave 12.6 of 93% pure $\text{ICF}_2\text{CF}_2\text{COF}$, bp $58-63^\circ\text{C}$, 6.0 g of a mixture of $\text{ICF}_2\text{CF}_2\text{COF}$ and $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$, bp $26-100^\circ\text{C}/200$ mmHg, 17.9 g of $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$, bp $100-102^\circ\text{C}/200$ mm Hg, 16.7 g of a mixture of 75% $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ and 16% $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ and 4.3 g of $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$. ^{19}F NMR for $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$: +45.5 (m, 1F), -58.7 (dm, J = 213.7 Hz, 2F), -60.0 (dm, J = 214 Hz, 2F), -76.9 (m, 3F), -77.9 (dd, J = 139.2 Hz, J = 22.7 Hz, 1F), -79.7 (dm, J = 139.2 Hz, 1F), -122.2 (s, 2F), -133.6 (m, 1F).

What is claimed is:

1. A process for making diiodofluorinated compounds of the formula $\text{ICF}_2(\text{A})_n\text{I}$ wherein n is an integer of at least 1 and each A is CXYCQZ wherein each X , Y , Q , and Z are each independently selected from the group consisting of H , F , Cl , R_F and OR_F , and R_F is a perfluoroalkyl group containing 1 to 20 carbon atoms or a perfluorinated polyether group containing from 2 to 20 carbon atoms wherein one or more of the fluorines of said perfluoroalkyl or perfluorinated polyether group is optionally replaced by a substituent selected from the group consisting of chlorine, bromine, iodine, hydrogen, sulfonyl fluoride, nitrile, ester, acyl chloride and acyl fluoride, comprising:
 - reacting an olefin of the formula $\text{CXY}=\text{CQZ}$ with CF_2I_2 at a temperature in the range of from about 120°C to 240°C .
2. The process of Claim 1 wherein the temperature is between about 170°C and about 190°C .
3. The process of Claim 1 wherein n is 1 to 5.
4. The process of Claim 1 wherein n is 1 to 3.
5. The process of Claim 1 wherein n is 1.
6. The process of Claim 1 where X and Y are each F .
7. The process of Claim 6 wherein the olefin is selected from the group consisting of $\text{CF}_2=\text{CFH}$, $\text{CF}_2=\text{CFCF}_3$ and $\text{CF}_2=\text{CH}_2$.
8. The process of Claim 1 wherein the olefin is $\text{CF}_2=\text{CF}_2$ or $\text{CF}_2=\text{CFCl}$.
9. The process of Claim 1 wherein the olefin is a perfluorovinylether of the formula $\text{CF}_2=\text{CFOR}_\text{F}$.
10. A diiodofluorinated compound of formula:



- wherein R_F is a perfluoroalkyl group containing 1 to 20 carbon atoms or a perfluorinated polyether group containing from 2 to 20 carbon atoms wherein one or more of the fluorines of said perfluoroalkyl or perfluorinated polyether group is optionally replaced by a substituent selected from the group consisting of chlorine, bromine, iodine, hydrogen, sulfonyl fluoride, nitrile, ester, acyl chloride and acyl fluoride.

INTERNATIONAL SEARCH REPORT

Inter. Appl. No.
PCT/US 97/08166

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C17/278 C07C17/275 C07C19/16 C07C41/30 C07C43/12
C07B37/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 926 411 A (PENNSALT CHEMICALS CORPORATION) 15 May 1963 see example 7	1-3,6,7
A	US 2 551 639 A (C.F. FEASLEY ET AL.) 8 May 1951 see claims	1
A	J. ORG. CHEM. (JOCEAH,00223263);84; VOL.49 (1); PP.205-7, UNIV. FLORIDA;DEP. CHEM.; GAINESVILLE; 32611; FL; USA (US), XP002039805 ELSHEIMER S ET AL: "Difluorodiodomethane: its preparation, properties and free-radical reactions" cited in the application see the whole document	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

5 September 1997

Date of mailing of the international search report

15.09.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Bonnevalle, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inten. .nal Application No

PCT/US 97/08166

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 926411 A		DE 1274581 B FR 1231263 A GB 926412 A	28-09-60
US 2551639 A	08-05-51	NONE	

THIS PAGE RI ANK 115077

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)